ON

A NEW MODE OF FORMING COMPOUNDS OF METALS WITH THE SULPHUR AND PHOSPHORUS GROUPS.

INAUGURAL DISSERTATION

FOR THE

DEGREE OF DOCTOR OF PHILOSOPHY,

AT THE

Georgia Augusta University,

IN GÖTTINGEN.

BY

THEODORE PARKMAN,

OF NEW YORK.

ACAD. LUGD. BAT. BIBL.

GÖTTINGEN:

PRINTED AT THE UNIVERSITY PRESS,

BY E. A. HUTH.

1860.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41544709_0090

The subject of the following dissertation was suggested by an observation made in the laboratory of Prof. Wöhler, at Göttingen. In precipitating selenium, by sulphurous acid, from a solution which contained considerable copper, the selenium obtained was black, although the precipitation took place in the cold. On investigation, the selenium was found to contain copper. My honoured instructor, Prof. Wöhler, suggested to me that, as this reaction was a new and somewhat singular one, to extend it to tellurium, sulphur, phosphorus, arsenic and antimony, might afford the matter for a not uninteresting investigation. I take the opportunity here to express my hearty thanks to Prof. Wöhler for his kind assistance in the present work, as well as during the rest of the time that I have worked in his laboratory.

I. ACTION OF SULPHUR ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

As already mentioned, precipitated selenium, placed in a solution of sulphate of copper containing sulphurous acid, unites with copper. I find that sulphur, tellurium, phosphorus, arsenic and antimony all do the same. In most cases also, the same effect is produced, especially with the aid of heat, without the presence of sulphurous acid or other reducing agent. I have also extended the investigation, though less completely, to the salts of silver and lead. With the exception of the action of phosphorus on the copper and silver solutions, all these reactions appear to have been previously undescribed.

1. ACTION OF SULPHUR WITHOUT THE AID OF REDUCING AGENTS.

Precipitated sulphur and flowers of sulphur were left a week in solutions of sulphate, acetate and chloride of copper. At the end of that time, they were entirely unchanged. Precipitated sulphur, boiled five or six hours with the sulphate, was slightly blackened, from formation of sulphide. Precipitated sulphur and flowers of sulphur, boiled with the acetate, rapidly blackened and were finally, apparently, entirely converted into

sulphide of copper. Sulphur *, left three days in solution of nitrate of silver, became dark grey. Boiled in solution of nitrate of silver, it became rapidly black and seemed to be entirely converted into sulphide of silver. Sulphur, boiled with acetate of lead, only by very long boiling became dark grey.

2. ACTION OF SULPHUR WITH THE AID OF REDUCING AGENTS.

Sulphur, left for some hours in solutions of sulphate, acetate and chloride of copper, with which sulphurous acid was mixed, became gradually dark grey, from formation of sulphide. Left a week in similar solutions, it appeared to be almost entirely converted into dark blue, or black sulphide of copper. By boiling the solutions, the reaction took place much more rapidly, the sulphur becoming black in a few minutes. Sulphur, green vitriol and sulphate of copper, boiled together, gave rapidly sulphide of copper. Sulphur, zinc and sulphate of copper, boiled together, gave, along with reduced copper, black sulphide.

Sulphur, boiled with acetate of lead and acetate of the protoxyd of iron, became rapidly black and was apparently completely converted into sulphide. The resulting sulphide contained no iron.

3. ANALYSIS OF THE PRODUCTS OF THE FOREGOING REACTIONS.

In preparing the above substances for analysis, my great care was to continue the action long enough to

* In all the following experiments the sulphur used was precipitated by sulphuric acid from hyposulphite of soda.

be sure that all the sulphur was converted into sulphide. In those prepared by simply boiling the sulphur with the solution of the metal, the boiling was continued from five to eight hours, in every case with an excess of the metallic salt. In preparing the sulphides by the aid of sulphurous acid, the sulphur was placed in the solution of the metal, the whole heated, though not to boiling, and then saturated with sulphurous acid gas. The solution was then boiled, allowed to cool, again saturated with sulphurous acid, and left to stand a couple of days in a closed flask. In every case, on opening the flask, there was still an excess of the metallic salt and of sulphurous acid. To prevent oxydation, the substances, during washing, were kept covered with water, as much as possible, and dried in vacuo. In none of then could any free sulphur be seen by the aid of the lens. Of each substance two preparations were made, in order to see if the composition of the substance remained constant.

For analysis, the substances were all dissolved by digestion with fuming nitric acid, which, in nearly every case, dissolved them up completely, without separation of sulphur. The analyses of the copper compounds were made, in some cases, by precipitating the oxyd of copper, at the boiling point, by caustic potash, and the sulphuric acid from the filtrate, after acidulation, by chloride of barium. In other cases, separate portions of substance were taken for the copper and sulphur determinations. The silver compounds were all analyzed by precipitating, first the silver by hydrochloric acid, and then the sulphuric acid, from the filtrate, by chloride of barium

SULPHIDE OF COPPER PREPARED BY BOILING SULPHUR WITH ACETATE OF COPPER.

First preparation. 0.6946 grm. substance gave 0.2817 oxyd of copper and 2.6436 sulphate of baryta.

Second preparation. 0.3255 grm. substance gave 0.1479 oxyd of copper and 1.2938 sulphate of baryta.

	I.	II.
Cu	32.37	36.28
S	52.27	54.56
	84.64	90.84

SULPHIDE OF COPPER OBTAINED BY THE AID OF SULPHUROUS ACID.

First preparation.
I. 1.9560 grms. substance gave 1.3145 oxyd of copper.
II. 1.7321 grms. substance gave 1.1615 oxyd of copper.
III. 0.6727 grm. substance gave 2.0356 sulphate of baryta.

Second preparation.
I. 1.8346 grms. substance gave 1.4830 oxyd of copper. *
II. 2.2385 grms. substance gave 5.4626 sulphate of baryta.

* According to Rose (Analytische Chemie II. 187) in igniting oxyd of copper, the filter may be burned along with the precipitate, and any suboxyd formed may be reoxydized by means of the current of air, which may be directed into the crucible by means of the cover. This is probably true in most cases, but sometimes there may be considerable loss through reduction. In the above analysis, after weighing once, I ignited and weighed again. The substance had increased considerably; and only after

			I. III.	II.
1st Prep.	Cu		53.76	53.54
	S		41.54	
			95.30	

				Calculated.	I. II. Found.
2nd Prep.	Cu	31.7		66.46	64.54
	S	16.		33.54	33.51
		47.7		100.00	98.05

SULPHIDE OF SILVER PREPARED BY BOILING SULPHUR WITH NITRATE OF SILVER.

First preparation. I. 2.0266 grms. substance gave 1.6800 chloride of silver and 4.9156 sulphate of baryta.
II. 1.3725 grms. substance gave 1.1359 chloride of silver and 3.2839 sulphate of baryta.

Second preparation. 0.4670 grm. substance gave 0.3519 chloride of silver and 1.4593 sulphate of baryta.

ignition, in a current of air, of three or four hours, in all, and a total increase in weight, from the first weighing to the last, of 0.0568 grm. (= 3.1 per cent. of the substance analyzed) was a constant weight obtained. On breaking up the lumps of oxyd of copper, some red suboxyd still remained, which had been protected from oxydation by the coat of protoxyd on the outside. This would account, in part, at any rate, for the percentage of copper in the above analysis coming out too low. It is decidedly advisable to burn the filter separately. This was done in my other analyses, with one exception, in which, from its close correspondence with an other analysis, little or no loss appeared to have been incurred.

		I.	II.
1st Prep.	Ag	62.39	62.28
	S	33.31	32.86
		95.70	95.14

			Calculated.	Found.
2nd Prep.	Ag	108	57.45	56.70
	5 S	80	42.55	42.91
		188	100.00	99.61

The formula Cu S, derived from one of the above analyses is probable enough. The formula $Ag S^5$ is not a probable one, and the substance may perhaps be a mixture of the ordinary sulphide of silver with unchanged sulphur. No sulphur, however, could be seen by the aid of a lens. The substance was apparently a perfectly homogeneous, dark-grey powder. Lumps of it, when crushed, had the same appearance.

It will be seen that, in the analyses of the above substances, two preparations excepted, there is a large loss, if the substances be supposed to consist only of sulphur and metal. That this loss is not owing merely to incorrect analyses is shown by the pretty close correspondence of the analyses of the first preparation of sulphide of silver and of two of the copper determinations. I at first supposed that the sulphides had partly oxydized to sulphates: but, on heating them, first with water and then with dilute sulphuric acid, either none at all or only a trace was dissolved. Any sulphate, or other salt of silver or copper with the sulphur acids, should have dissolved up in the dilute acid. Heated in a dry test-tube, none of the substances gave any water. These facts led me to suppose that perhaps the presence of an oxysulphide, either alone, or mixed with a sulphide,

might not be impossible. On examining the analyses in which there was a loss, I find that the analysis of one of the sulphides of copper corresponds closely to the formula $CuOS^3$. *

		Calculated.	Found.
Cu	31.7	36.15	36.28
O	8.	9.12	
3 S	48.	54.73	54.56
	87.7	100.00	

This formula is not very probable, and I regret that I had not the time to investigate the subject further.

The analyses of the other sulphides did not correspond to any formula. When carefully examined under a lens, the copper compounds appeared to contain two substances. At first they appeared to be simply composed of a deep blue or blue-black powder. On breaking some of the lumps, however, these latter were found in many cases to be composed of a hard, light coloured substance, with a reddish tinge and somewhat metallic appearance. Its appearance was very much like that of protosulphide of iron, which has been fused and then broken. The substance, which corresponded to the formula $CuOS^3$, was almost perfectly homogeneous and

* The oxysulphides already described are ZnO, ZnS, CoO, CoS, and MnO, MnS, described by Arfvedson (Pogg. 1.), AsO^3S^2 by Bouquet and Cloez (N. Ann. de Chim. et Phys. 13. 14. J. der Pharm. 7. 23), and red antimony-ore, $SbO^3, 2SbS^3$. Of all these, the only one, the composition of which bears much resemblance to the formula ($CuOS^3$), is the arsenic compound; and from the wide dissimilarity between arsenic and copper, this analogy is of but little value as a proof of the probability of the above formula.

was different in colour from the other copper compounds. It was dark grey, nearly black, without the bluish tinge of the others. The sulphides of silver were dark grey, one nearly black, the other considerably lighter. Both appeared to be perfectly homogeneous.

With regard to the manner in which the sulphides are forming by boiling sulphur with the salts of silver and copper, it might be supposed that one portion of the sulphur would be oxydized at the expense of the oxyd of the metal, while another portion of sulphur would unite with the metal, thus set free. Whether this is the case, or not, appears to be somewhat doubtful. After boiling sulphur a long time with solutions of acetate of copper and nitrate of silver, until the sulphur was well blackened, the filtrates were tested for sulphuric acid. In the copper solution none was found: in the silver only a trace. Another portion of each filtrate was then tested for other acids of sulphur, by boiling with nitric acid and then adding chloride of barium. No sulphur separated, on adding the acid, and chloride of barium gave merely a trace of sulphate of baryta in the silver solution: none in the copper solution. It is possible that the sulphur may be oxydized to sulphurous acid. No smell of this could be detected, during boiling; but as the action of the sulphur is not very rapid, the sulphurous acid may have been given off in too small quantity to have been detected. Against this hypothesis, however, are the following considerations. As has been shown, sulphurous acid and other reducing agents greatly assist the formation of the sulphides, and this can be owing only to their reducing power. Now, if the sulphur be oxydized to sulphurous acid, some of this latter would be oxydized to sulphuric acid, of which, in the copper solution at least, not a trace could

be detected. If the sulphur is not oxydized and no reducing agent be present, it would seem that one of two suppositions must be adopted: either the sulphur sets the oxygen of the oxyd free, which, I take it, is highly improbable, or the oxygen still remains in combination with the metal and an oxysulphide is formed. The substances no doubt vary with the circumstances under which they are formed — length of time in boiling, concentration of solution, &c. — since two of the analyses made agree with the formulas of sulphides, without oxygen. One of these was formed with the aid of sulphurous acid. In the other, it may be supposed that the sulphur perhaps in this case acted as a reducing agent.

II. ACTION OF SULPHUROUS ACID ON THE SOLUTIONS OF COPPER.

As sulphurous acid was used in forming several of the compounds above described, I deemed it advisable to make some investigation into the action of sulphurous acid alone on the solutions of copper used.

Sulphurous acid in most cases produces no effect on the compounds of copper with the stronger acids. Under certain circumstances, however, a solution of sulphate of copper gives with sulphurous acid a small quantity of the well-known red sulphtie of protoxyd and suboxyd of copper ($CuO, SO^2 + Cu^2O, SO^2 + HO$, Rammelsberg), and in other cases small crystals of metallic copper. *

* Wöhler, Ann. der Chem. u. Pharm. 79. 126—127.

The action of sulphurous acid upon acetate of copper does not appear to have yet been observed. I found that sulphurous acid gas passed through a solution of acetate of copper, heated, though not to boiling, gave at first a yellowish precipitate. This dissolved up again as the operation was continued, and the solution deposited a large quantity of small, bright red crystals. The reactions of these corresponded to those of the red sulphite, mentioned above. This gives, therefore, a new method of preparing the above salt.

The yellowish precipitate, just mentioned, may also be obtained by adding sulphurous acid water, in small quantity, to a solution of acetate of copper, which contains little or no free acid. After washing and drying it was of a yellow colour, with a slight greenish tinge. It appeared to be entirely insoluble in water. No crystals could be detected by the lens.

With sulphuric acid it gave off sulphurous acid in large quantity. By solution of caustic potash it was converted into a bright green, insoluble substance. (See further on). By boiling with caustic potash, it gave black oxyd of copper. A portion, dried in vacuo, over sulphuric acid, gave off considerable water, on heating in a closed tube. It was found to contain no alkali, and no acetic acid.

For analysis, the salt was boiled with chlorine water until it dissolved, the sulphuric acid precipitated by chloride of barium, the excess of chloride of barium by sulphuric acid, and the oxyd of copper, at the boiling point, by caustic potash.

1.2266 grms. substance gave 1.0341 sulphate of baryta and 0.6975 oxyd of copper.

		Calculated.	Found.
$2CuO$	79.4	57.37	56.86
SO^2	32.	23.12	23.15
$3HO$	27.	19.51	
	138.4	100.00	

The salt is very soluble in sulphurous acid, to a green solution. The latter, by standing, deposits the red sulphite. Acetic acid has a precisely similar effect. In preparing the salt, therefore, the solution of acetate of copper must be neutral and the sulphurous acid added in small quantity. If too much acid be added, the precipitate will be redissolved, even before the solution smells of sulphurous acid.

The salt appears to be until now undescribed. The only mention I can find of anything similar is in a paper on the sulphites, by Böttinger.

Böttinger *, by mixing a solution of sulphate of copper with sulphite of ammonia containing but a small quantity of free sulphurous acid, obtained a dirty greenish-yellow precipitate, which, on the addition of a little sulphurous acid, was rapidly and easily converted into a beautiful green liquid. This yellow precipitate he did not investigate further. I prepared a quantity of it for comparison with the salt which I obtained. The colour of the two substances varied considerably from each other. That obtained by means of sulphite of ammonia was brownish-yellow, with little or no greenish tinge. That prepared from acetate of copper was of a much brighter yellow, with a decided tinge of green. Böttinger's salt, however, gave precisely the same reactions as mine. With strong acids it gave off

* Ann. der Chem. u. Pharm. 51. 410.

sulphurous acid in large quantity. With caustic potash it became bright green. By boiling with caustic potash it became black and gave no smell of ammonia. The two salts, therefore, are no doubt identical.

The salt, just described, gave, with excess of caustic potash, a bright green insoluble substance, entirely different in appearance from the ordinary blue hydrated oxyd of copper. Boiled with caustic potash, it was rapidly and entirely converted into black oxyd of copper. Dissolved in strong boiling nitric acid, it did not give the slightest reaction with chloride of barium. By long washing, it gradually lost its green colour and finally became light greyish blue.

For analysis, a portion was washed slightly, until the wash-water was no longer alkaline, and dried in vacuo. After drying, it was of a lighter green than while moist. A portion dissolved up in hydrochloric acid, without escape of carbonic acid. A weighed portion was ignited in a platinum crucible, the weight of the substance, after ignition, calculated as oxyd of copper, and the loss of weight as water. The oxyd of copper, after weighing, was washed and again weighed, to ascertain whether it contained alkali. The loss in weight after washing amounted to only 0.0008 grm., so that any alkali present is merely as an impurity.

0.3215 grm. substance weighed after ignition, 0.2428. Loss = 0.0787.

		Calculated.	Found.
2 CuO	79.4	74.62	75.52
3 HO	27.	25.38	24.48
	106.4	100.00	100.00

The greyish blue substance, obtained from the green hydrated oxyd by long washing, analyzed in the same way, gave the following result:

0.4042 grm. substance, after ignition, weighed 0.3228. Loss = 0.0814.

	Calculated from 2 CuO, 3 HO	Calculated from CuO, HO	Found.
CuO	74.62	81,52	79.86
HO	25.38	18.48	20.13
	100.00	100.00	99.99

The green hydrated oxyd, therefore, would appear to be almost entirely converted, by long washing, into the ordinary hydrated oxyd. It dissolved in hydrochloric acid, without escape of carbonic acid.

From the result of the above analyses, it seems to be certain that the green substance is a hydrated oxyd of copper, containing more water than the ordinary blue hydrate. Owing to the substance losing its water so readily, it is perhaps hardly certain that it has the formula which I have given. The analysis, however, corresponds closely enough to make it highly probable. The number of atoms of oxyd of copper and water in the formula 2 CuO, 3 HO, it will be seen, corresponds with that in the salt ($2\,CuO, SO^2, +3\,HO$) from which it was obtained. Not improbably the cause of its formation may have something to do with this fact.

The only mention that I can find of any hydrated oxyd of copper containing more than one atom of water is in the following extract from Gmelin's Chemistry. "According to Fremy (N. Ann. de Chim. et Phys. 23. 161) hydrated cupric oxyd obtained by precipitating a solution of blue vitriol in the cold with a large excess of potash, and then drying in vacuo, contains CuO, + 2HO". I did not have an opportunity of referring to Fremy's paper; but I presume that the oxyd that he obtained was not the green hydrate, just described. I precipitated a solution of blue vitriol with large excess of caustic alkali, and the precipitate did not differ at all in appearance from the ordinary blue hydrate.

III. ACTION OF RED SELENIUM ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

1. WITHOUT THE PRESENCE OF REDUCING AGENTS.

Red selenium, left four days in solutions of sulphate and acetate of copper, still remained red, showing that it had not combined with copper. The same, boiled with sulphate of copper, for a long time, did not take up any copper. Boiled with acetate of copper, however, it was found to have united with considerable copper.

For analysis of the product of this last reaction, red selenium was boiled several hours with acetate of copper, thoroughly washed, and dried in vacuo. The substance obtained was a black powder, mixed with hard lumps, which, when broken; had a somewhat metallic lustre. For analysis, it was dissolved in nitric acid, the oxyd of copper precipitated, at the boiling point, by caustic potash, washed, dried, and ignited with saltpetre and carbonate of potash.

0.5237 grm. substance gave 0.0507 oxyd of copper.

		Equivalents.
Cu	7.73	1
Se (by difference)	92.27	9.7
	100.00	

Hence it would seem that the selenium was only partly converted into selenide of copper, notwithstanding that the boiling was kept up five hours, or more.

Red selenium, left four days in solution of nitrate of silver, gave a black powder, along with a few white flakes of (probably) selenious acid. After dissolving out the latter by means of caustic soda, the black powder was found to contain selenium and silver, both in large quantity. No free selenium could be seen in it, by the aid of the lens. (See remarks on the action of tellurium on nitrate of silver.)

Red selenium, boiled a long time with acetate of lead, took up no lead.

2. WITH THE AID OF REDUCING AGENTS.

As already mentioned, red selenium, with sulphate

of copper and sulphurous acid, becomes black, through formation of selenide of copper.

For analysis, a portion was prepared in the same manner as the corresponding sulphide of copper. The product obtained was a black powder, nearly homogeneous, but containing a few glistening particles, which looked like metallic copper. The substance was dissolved in nitric acid and the oxyd of copper precipitated as usual by caustic potash. The separation of copper and selenium in this manner is not quite perfect, a little selenious acid being usually precipitated, along with the oxyd of copper. Accordingly, the copper in the following analysis comes out somewhat too high.

1.0735 grms. substance gave 0.8336 oxyd of copper.

		Calculated.	Found.
2 Cu	63.4	61.61	62.00
Se	39.5	38.39	
	102.9	100.00	

This same compound may also be formed by heating copper with selenium, or by igniting the protoselenide in a close vessel. (Berzelius.) It is also found native.

Red selenium, boiled half an hour with acetate of lead and acetate of the protoxyd of iron, did not take up any lead.

IV. ACTION OF PRECIPITATED TELLURIUM ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

1. WITHOUT THE AID OF REDUCING AGENTS.

Precipitated tellurium, left four days in solutions of sulphate and acetate of copper, did not unite with any copper. Boiled with sulphate of copper, four or five hours, it also remained unchanged. Boiled with acetate of copper, it took up considerable copper. Some of the product of this action, obtained by boiling the tellurium four or five hours with the acetate, consisted of a black powder, containing a few glistening particles, otherwise homogeneous. An analysis of it was made as follows. The substance was dissolved in aqua regia and the oxyd of copper precipitated by caustic potash, dried, and ignited with nitre and carbonate of potash. To free the oxyd entirely from tellurous acid, it was again boiled with caustic potash, After weighing, the oxyd of copper was tested for tellurium and was still found to contain a trace.

0.2671 grm. substance gave 0.0831 oxyd of copper.

		Calculated.	Found.
2 Cu	63.4	24.82	24.82
3 Te	192.	75.18	
	255.4	100.00	

This and the following are, I believe, the only analyses that have been made of a telluride of copper.

Gmelin (Handbook of Chem. Engl. Transl.) merely mentions that telluride of copppr is pale red, according to Berzelius.

The action of tellurium upon nitrate of silver has been observed by Fischer: viz. that it acts very freely upon the solution of nitrate of silver, and forms a black powder, which does not assume the metallic lustre under pressure. Fischer does not mention whether the black powder was telluride of silver or metallic silver, but leaves it to be inferred that it was the latter, as the observation is given in connection with the reducing action of the metals upon the salts of silver. That telluride of silver is formed is probable from the analogous action of sulphur upon nitrate of silver, as well as of selenium and tellurium on acetate of copper. The following experiment also makes this probable. Precipitated tellurium was left four days in solution of nitrate of silver. At the end of that time, the solution still contained a large excess of silver. The black powder appeared under the lens to be perfectly homogeneous and to contain no white flakes of tellurous acid. It was found to contain silver and tellurium, both in large quantity. Now, if the silver was precipitated metallic by the tellurium, probably little or no tellurium would remain unoxydized, after being in contact so long with an excess of the silver solution, but would either pass entirely into solution (the hydrate of tellurous acid dissolves in water with tolerable facility. Berzelius) or, if there was not enough liquid present to dissolve the whole, be visible as white tellurous acid.

Precipitated tellurium, boiled a long time with acetate of lead, precipitated no lead.

2. WITH THE AID OF REDUCING AGENTS.

Precipitated tellurium, heated with sulphate of copper and sulphurous acid, united with considerable copper. For analysis of the product of this reaction, a portion was prepared in the same manner as the corresponding sulphide of copper. The substance obtained was a black powder. It was ignited with nitre and carbonate of soda, and the oxyd of copper separated from the melted mass by dissolving in water. This method is not to be recommended. The platinum crucible used was attacked somewhat (perhaps because there was not enough nitre), and platinum was thus mixed with the oxyd of copper. To separate them, the oxyd of copper was ignited a long time, to bring all the platinum into the metallic state, and then dissolved out with nitric acid and precipitated by caustic potash. A better mode of analysis is that given in the analysis last described.

0.9498 grm. substance gave 0.3818 oxyd of copper.

		Calculated.	Found.
Cu	31.7	33.12	32.09
Te	64.	66.88	
	95.7	100.00	

Precipitated tellurium, boiled half an hour with acetate of lead and acetate of the protoxyd of iron, did not combine with any lead.

V. ACTION OF PHOSPHORUS ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

1. WITHOUT THE PRESENCE OF REDUCING AGENTS.

The action of phosphorus on solutions of copper has already been observed by Bœck, Vogel and Bœttcher, and I have but little new to add to their observations. The following are the reactions of phosphorus on the most important salts of copper, as observed by Vogel.* In a close vessel, the sulphate becomes decolorized in a few days and the phosphorus is covered with a shining coating of copper. After some months, a black deposit of phosphide of copper is found between this film and the remaining phosphorus. On the nitrate, in closed vessels, the action is nearly the same. Very bright metallic copper is deposited, and so large a quantity of phosphide formed, that the remaining phosphorus is blackened by it throughout its whole substance. A dilute solution of the acetate, kept in contact with phosphorus in a closed vessel, becomes paler, deposits greenish-white flakes of phosphate of copper, and covers the phosphorus, first with a black and then with a copper-coloured deposit. In a dilute solution of protochloride of copper, phosphorus becomes covered with metallic copper; but in a concentrated solution, it first produces an abundant precipitation of white subchloride of copper, and then becomes blackened throughout its substance by phosphide of copper.

* Journal für praktische Chemie. Vol. III.

Phosphorus, placed in a boiling solution of sulphate of copper, gave at first metallic copper, but this gradually blackened and by continued boiling appeared to be entirely converted into phosphide. This has been also observed by Böttcher. For analysis, I prepared some of the above phosphide by boiling phosphorus five or six hours with sulphate of copper. The substance obtained was a black powder, the larger particles possessing considerable lustre. Under the lens it appeared to be perfectly homogeneous. Even when finely pulverized, not a trace of metallic copper could be seen. Heated on platinum foil, here and there a very slight flame was observed for two or three seconds. The quantity of free phosphorus, however, if there was any present, must have been extremely small.

For analysis, a portion was dissolved in hydrochloric acid, with the aid of chlorate of potash, the solution heated until it no longer smelled of chlorine, diluted, and the copper precipitated by sulphuretted hydrogen. The filtrate was saturated with ammonia, and the phosphoric acid precipitated by sulphate of magnesia (mixed with chloride of ammonium in sufficient quantity to prevent its precipitation by ammonia). The sulphide of copper was dissolved in fuming nitric acid and the oxyd precipitated by caustic potash.

0.6695 grm. substance gave 0.7301 oxyd of copper and 0.2916 phosphate of ammonia-magnesia.

		Calculated.	Found.
7Cu	221.9	87.74	87.06
P	31.	12.26	12.16
	252.9	100.00	99.22

The phosphides of copper previously described are Cu^6P, Cu^3P and Cu^2P.

Phosphorus in solution of nitrate of silver throws down metallic silver, as observed by Bœck. The silver has the usual colour and metallic lustre, and is apparently crystalline. No phosphide could be seen.

Phosphorus, left three days with a solution of acetate of lead in a closed test-tube, gave merely a few white flakes, probably of phosphate of lead. On boiling, a black precipitate was rapidly formed in large quantity, along with white phosphate of lead. After dissolving out the latter with caustic potash, the black substance was dissolved up in nitric acid, and tested for phosphoric acid. None was found: so that the substance, it would seem, was metallic lead.

2. IN THE PRESENCE OF REDUCING AGENTS.

Solution of sulphate of copper was saturated with sulphurous acid, phosphorus added, the whole heated somewhat, and left three days in a closed flask. On opening the flask, the solution was colourless. The result was metallic copper, and black phosphide of copper, along with unchanged phosphorus. I did not attempt to analyze the phosphide, as it was so intimately mixed with finely divided metallic copper that it was impossible to obtain it pure.

VI. ACTION OF ARSENIC ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

1. WITHOUT THE AID OF REDUCING AGENTS.

Pulverized metallic arsenic, boiled with sulphate of copper, took up considerable copper. For analysis of the product of this reaction, pure metallic arsenic, pretty finely pulverized, was boiled several hours with concentrated solution of sulphate of copper. The substance obtained was a perfectly homogeneous, dark-grey powder. It was dissolved up in hydrochloric acid, with the aid of chlorate of potash, and digested at a very gentle heat with excess of chlorate of potash, in order to make sure of converting all the arsenic into arsenic acid, until the solution was nearly free from chlorine. The solution was then made strongly alkaline with ammonia and the arsenic acid precipitated by a mixture of sulphate of magnesia and chloride of ammonium. This was washed with water, containing considerable ammonia, brought upon a weighed filter and dried at 100° C. From the filtrate, after acidulation, the copper was precipitated by sulphuretted hydrogen, dissolved in fuming nitric acid and reprecipitated by caustic potash.

1.0225 grms. gave 0.7211 arseniate of ammonia magnesia ($2MgO, NH^4O, AsO^5, + HO$) and 0.9276 oxyd of copper.

		Calculated.	Found.
6 Cu	190.2	71.72	72.43
As	75.	28.28	27.83
	265.2	100.00	100.26

The arsenides of copper previously described are Cu^4As and Cu^3As.

Arsenic in solution of nitrate of silver throws down metallic silver, as already observed by Fischer.

2. WITH THE AID OF REDUCING AGENTS.

Pulverized metallic arsenic, heated with solution of sulphate of copper and sulphurous acid, forms arsenide of copper. For analysis, a portion was prepared in the same manner as the corresponding sulphide of copper. The substance obtained was a dark-grey, perfectly homogeneous powder. Two arsenic determinations were made, in the same way as in the last analysis.

I. 1.1215 grms. substance gave 1.4189 $2MgO, NH^4O, AsO^5, + 12HO$ (dried in vacuo).

II. 0.3235 grm. substance gave 0.2650 $2MgO, NH^4O, AsO^5 + HO$ (dried at 100° C.).

		Calculated.	Found. I.	Found. II.
5Cu	158.5	67.88		
As	75.	32.12	32.78	32.33
	233.5	100.00		

Pulverized arsenic, boiled half an hour with acetate of lead, precipitated no lead. With acetate of the protoxyd of iron and acetate of lead, it also produced no effect.

VII. ACTION OF ANTIMONY ON THE SOLUTIONS OF COPPER, SILVER AND LEAD.

1. WITHOUT REDUCING AGENTS.

Pulverized antimony, left three days in solutions of sulphate and acetate of copper, took up considerable copper, in both cases. A little white oxyd of antimony was also formed. By boiling, the action takes place more rapidly, and a large quantity of the oxyd is formed.

As already observed by Fischer, antimony precipitates metallic silver from the nitrate, Towards the end of the action, some antimonide of silver is also formed, according to Fischer.

Antimony, boiled a long time with acetate of lead, produced no effect.

2. WITH REDUCING AGENTS.

Pulverized antimony, left three days in solution of sulphate of copper, mixed with sulphurous acid, combined with considerable copper. No white oxyd could be seen. In acetate of copper the same effect was produced.

Antimony, boiled with acetate of the protoxyd of iron and acetate of lead, did not throw down any lead.

THE END.